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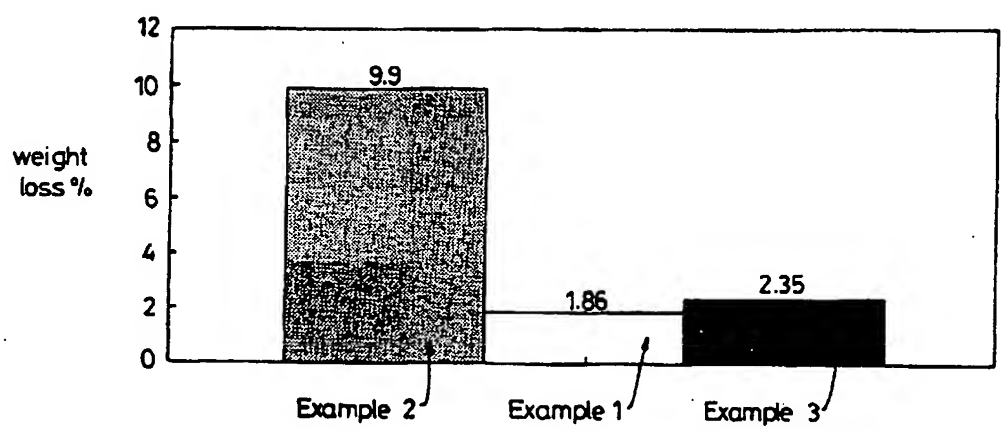

(57) Abstract

A process for the manufacture of fibre-reinforced synthetic resin article comprises the steps of forming an aqueous suspension of fibres by intimate blending of water-dispersible reinforcing fibres and web-forming in the absence of binder material and thereafter producing a shaped fibrous preform from said suspension by a vacuum-forming operation, followed by drying the preform.

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Improvements in and relating to composite articles

This invention relates to fibre-reinforced synthetic resin composite articles and in particular to a method of manufacturing the same.

For many years such articles have been manufactured by a variety of routes. One very common process is to take woven and/or non-woven fabric, impregnated with a thermosettable resin composition and then prepare an laminate structure from a number of pieces of impregnated fabric cut to an appropriate shape. This laminate structure is then pressed cured into a finished article, the press-curing action serving to unite the individual fabric pieces into a unitary structure. In another well-known process, shaped pieces of textile fabric are stacked in a mould cavity to which is then added a quantity of liquid resin. The fabric and the resin are then press-cured/moulded together into a finished laminated article. It has also been proposed to form a solution or dispersion of fibres in a liquid binder medium which is thereafter de-watered to form a preform which after drying, is placed into a mould cavity with a quantity of liquid resin and then press-cured into a finished article.

The first two processes just described are labour-intensive and result in significant quantities of waste which cannot be re-used. Also, where a laminate structure is built up from a series of layers, it is both difficult to achieve uniform impregnation with a relatively viscous liquid resin and to achieve an acceptable degree of homogeneity in the final product. The latter

will of course always retain a laminar structure and accordingly it will be vulnerable under some circumstances to de-lamination. In the case of vacuum preforming from a slurry containing a binder material, although much better homogeneity can be achieved, there remains the problem of securing uniform distribution of the resin matrix material, simply because of the presence of the binder material necessary to hold the fibres of the preform together both during and after drying. Additionally, waste material is not readily re-usable, also because of the binder content.

It is an object of the present invention to provide an improved process which at least minimises the above disadvantages.

According to the present invention, a process for the manufacture of a fibre-reinforced synthetic resin article comprises the steps of forming an aqueous suspension of fibres by intimate blending of water-dispersible reinforcing fibres and web forming fibres in the absence of a binder material, and thereafter producing a shaped fibrous preform from said suspension by a vacuum forming operation, followed by drying the preform.

Optionally, the suspension may contain a finely powdered thermosettable resin material, for example, a phenolic resin, so that the dried preform is ready for compression moulding directly into a shaped article. Alternatively, the dried preform can be impregnated with a liquid resin composition immediately prior to moulding it under heat and pressure into a shaped article.

Preferred reinforcing fibres include carbon fibres, staple aramid fibres and glass fibres. Other fibres may also be used, for example nickel coated carbon fibres to confer a degree of electrical conductivity. The web-forming fibre component may be cellulose, but for higher temperature applications, aramid fibre pulp is preferred. Where the thermosettable resin powder is incorporated during intimate blending of the fibre components to make the suspension, it should be selected so as to be inactive at the temperature subsequently used to dry the preform.

It has been found that the web-forming fibre content of the suspension should not be less than 5%, referred to the total weight of fibres present. However, the web-forming fibres may comprise as much as 50% of the total fibre content and by varying the proportions of the fibre components it is possible to vary the properties of the end product. Where the web-forming content is relatively large, it may be necessary to incorporate the resin component into the suspension as a powder, in order to ensure that the resin in thoroughly and uniformly dispersed. This is because relatively high proportions of web-forming fibres tend to result in a dense structure which is not easily impregnated with liquid resin.

Optionally, the suspension may also contain particulate fillers selected to modify the thermal, mechanical, friction and/or electrical properties of the finished shaped article. Suitable fillers include metal flakes, graphite, micas, barytes, glass microspheres and lubricants such as molybdenum disulphide, where necessary finely powdered to ensure dispersion.

Because there is no binder material in the suspension, impregnation with resin either by adding it during blending of the fibres or afterwards to the dried preform is more thorough, to the point that the final shaped article is essentially monolithic and exhibits superior uniformity of appearance and properties. Such uniformity is not possible using the traditional multi-layer lamination technique based on superposed layers of textile fabrics or non-woven fibrous mats, because of the difficult of achieving an acceptable degree of uniform impregnation. This difficulty is not significantly improved by pre-impregnating individual layers or by using "pre-preg" felts, because the end product is inevitably still a laminar structure and not monolithic, as is the product of the instant invention.

Surprisingly, it has been found that despite the complete omission of a binder material from the aqueous suspension, use of the intimate fibre blend just referred to results in a pre-form having both good handling strength and an extremely open

nature as regards subsequent impregnation with the liquid resin. Also, the lack of any binder in the preform means that any waste material can be re-cycled so that the overall level of waste with the improved process of this invention is minimal. It will be apparent the lack of binder in the aqueous dispersion also means that the dispersion can be kept for indefinite periods, although of course it will be necessary to agitate the suspension from time to time in order to prevent excessive settlement.

In order than the invention be better understood, samples were made according to the invention and according to two prior art formulations.

Example 1

A laminate was made by superposing phenolic resin impregnated woven asbestos fibre fabric sheets. The resultant assembly was press-cured in conventional manner to produce a composite sheet, from which were cut both samples for physical testing purposes and a number of samples for use as rotor vanes in a vacuum pump.

Example 2

The procedure just described was repeated, substituting for the woven asbestos fabric a non-asbestos fabric comprising blended yarns of glass and aramid fibres.

Example 3

An aqueous slurry was made comprising the following ingredients by weight:-

10% aramid fibre pulp
25% 3mm glass fibres
12% 6mm staple aramid fibre
3% graphite powder
50% powdered phenolic resin

These ingredients were intimately blended by stirring to produce a homogenous suspension. From this suspension, a number of rotor blade preforms were produced by vacuum forming onto a wire mesh faced mould, the mesh size being approximately 50 (½mm). The vacuum applied was in the range 15-25 inches of mercury and the thickness of the product was of the order of 1 inch. On removing the mould from the suspension, the shaped preform was readily removable by hand and had surprisingly good integrity. It was dried in an oven at a temperature below the activation temperature of the phenolic resin component. Temperatures in the range 40-50°C are typically used for this.

The dried preforms where placed into mould cavities and press-cured into rotor blades. Some of the latter were used as samples for physical testing in direct comparison with the samples prepared under Examples 1 and 2.

On physical testing, the properties of the composites made according to Examples 1, 2 and 3 were as given below.

Properties	Example 1	Example 2	Example 3
Density gcm $^{-3}$	1.70	1.53	1.43
Flexural Strength/MPa	120	190	170
Flexural Modulus/GPa	10.0	8.5	8.2
Coefficient Thermal Expansion/x 10^{-6} per °C	11.0	14.0	9.8

From the above, it is apparent that the physical properties of the composite articles manufactured according to the present invention were directly comparable with those of the prior art processes. However, on visual inspection it was immediately apparent that the samples made according to the present invention had a very much higher uniformity. This was confirmed by standard deviation checks on a number of samples. Product according to the invention exhibited much less variability in properties.

To further illustrate the invention, reference is directed to the

accompanying graph on which wear data (weight loss %) is plotted for equal time periods. In the graph, the block marked Example 2 represents the wear rate of the rotor blades made from a non-asbestos composite comprising layers of a woven textile fabric containing 7% by weight aramid fibres and the rest being glass fibre core strands overlaid with staple cellulose fibres (viscose) using the DREF spinning process. These fabric layers were laminated using phenolic resin to form a composite slab which was cut/machined into rotor blades.

The block marked Example 1 represents the wear rate for rotor blades made from a traditional asbestos cloth/phenolic resin laminate.

The block marked Example 3 represents the wear rate for rotor blades made according to the invention, as just described above.

All three sets of blades were tested in a vacuum pump running at 1100 rpm for 30 hours at a vacuum level of 21 inches of mercury.

It is clear from the graph that whilst the traditional material of Example 2 was the best, the non-asbestos material of Example 3 of this invention was directly comparable in performance. The non-asbestos material of Example 1 however suffered a much greater weight loss and was unacceptable.

The performance of the material according to the present invention was extremely good, both as regards resistance to wear and to delamination in service.

CLAIMS

1. A process for the manufacture of a fibre-reinforced synthetic resin article comprising the steps of forming an aqueous suspension of fibres by intimate blending of water-dispersible reinforcing fibres and web-forming fibres in the absence of binder material and thereafter producing a shaped fibrous preform from said suspension by a vacuum-forming operation, followed by drying the preform.

2. A process according to claim 1 wherein the web-forming fibres constitute from 5-50% of the total weight of fibres.

3. A process according to claim 1 or claim 2 wherein the suspension further comprises a finely powdered thermosettable resin material.

4. A process according to claim 3 wherein the finely powdered thermosettable resin material is a phenolic resin.

5. A process according to claim 3 or claim 4 wherein the aqueous suspension further comprises at least one particulate filler selected to modify the thermal, mechanical friction and/or electrical properties of the finished shaped article.

6. A process according to any of claims 2 to 5 wherein the dried preform is subjected to a press-curing treatment effective to convert it into a shaped composite article.

7. A process according to claim 1 or claim 2 wherein the dried preform is placed into a mould cavity together with a quantity of a liquid resin composition immediately prior to moulding it under heat and pressure into a shaped article.

8. A process according to any preceding claim wherein the reinforcing fibres comprise carbon fibres, aramid staple fibres and/or glass fibres.

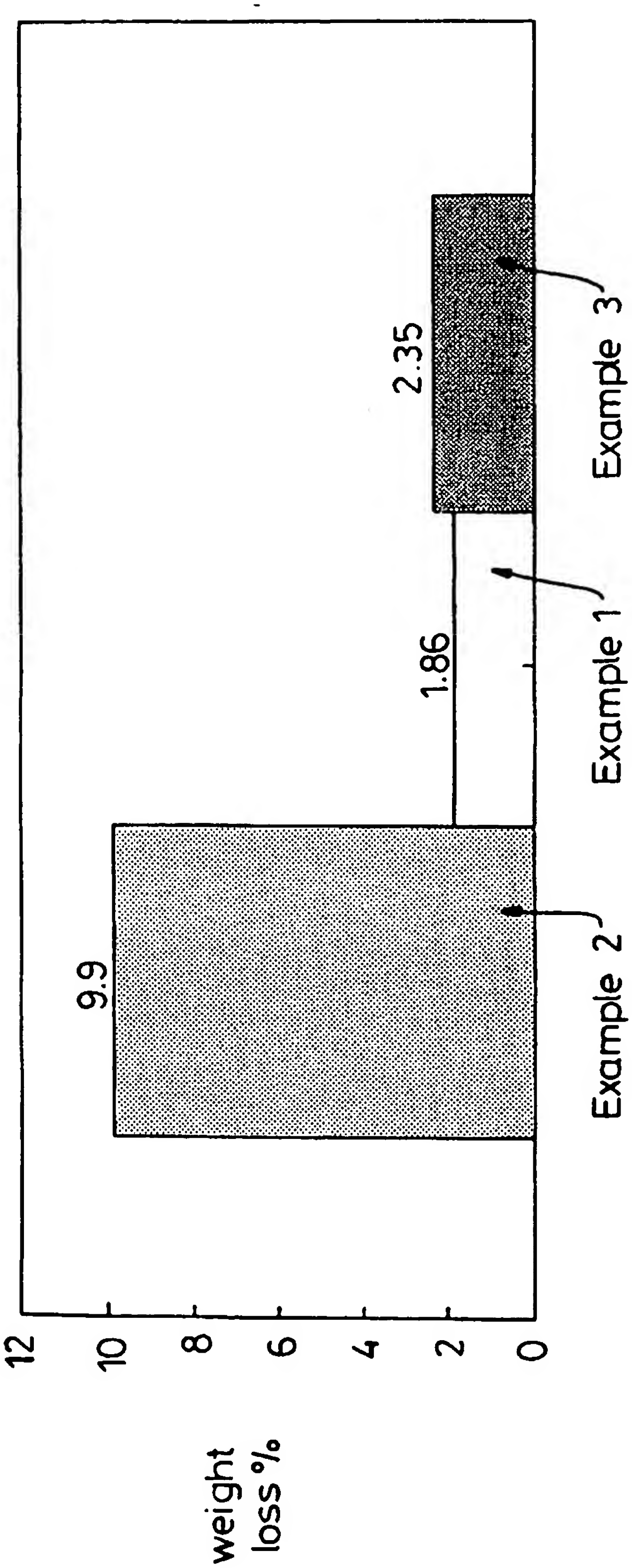
9. A process according to claim 8 wherein the reinforcing fibres further comprise organic fibres.

10. A process according to claim 9 wherein said organic fibres comprise staple aramid fibres.

11. A process according to preceding claim wherein the web-forming fibre component of the suspension comprises cellulose fibre pulp.

12. A process according to any of claims 1 to 11 wherein the web-forming fibre component comprises aramid fibre pulp.

13. A fibre-reinforced composite article made by a process according to any preceding claim.


weight
loss %
0
2
4
6
8
10
12
9.9
1.86
2.35
Example 2
Example 1
Example 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/01077

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J5/04 B29B11/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J B29B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 40 39 450 A (BAYER AG) 17 June 1992 see claims 1,2 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 406 (C-1090), 29 July 1993 & JP 05 078500 A (SHIN KOBE ELECTRIC MACH CO LTD), 30 March 1993, see abstract ---	1
A	WO 94 23125 A (EXXON CHEMICAL PATENTS INC ;JACOBS PAUL M (GB); DEVOREST YANN (US)) 13 October 1994 see claims 1,9 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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1

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	2244 RESEARCH DISCLOSURE April 1989, number 300, item 30017, page 246, Havant Hamphire, GB Disclosed anonymously "Process for the preparation of fibre-reinforced thermoplastic sheet" XP002039618 -----	1

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 97/01077

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4039450 A	17-06-92	NONE	
WO 9423125 A	13-10-94	EP 0738348 A	23-10-96